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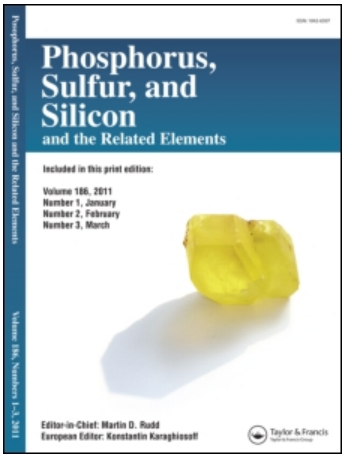

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SYNTHESES, CHARACTERIZATION AND REACTIVITY OF DIBENZOBICYCLIC PHOSPHORANES 10-P-5

Carlos Camacho-Camacho[a]; Francisco Javier Martínez-Martínez[b]; Maria De Jesús Rosales-Hoz[b]; Rosalinda Contreras[b]
[a] Departamento de Sistemas Biológicos, Universidad Autónoma Metropolitana Xochimilco, México, D.F. [b] Departamento de Química, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, México, D.F.

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SYNTHESES, CHARACTERIZATION AND REACTIVITY OF DIBENZOBICYCLIC PHOSPHORANES 10-P-5

CARLOS CAMACHO-CAMACHO,†
FRANCISCO JAVIER MARTÍNEZ-MARTÍNEZ,*
MARIA DE JESÚS ROSALES-HOZ* and
ROSALINDA CONTRERAS*

**Departamento de Química, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional. Apartado Postal 14-740, México 07000 D.F.;*
†Departamento de Sistemas Biológicos, Universidad Autónoma Metropolitana Xochimilco. Calzada del Hueso 1100, Col. Villa Quietud, México, 04960 D.F.

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Compound **1** has been prepared by demetallation with PCl_3 of *bis*[3,5-di-*tert*-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-*tert*-butylphenyl)imine] zinc complex **14**. Compound **1** has been shown to be an excellent precursor in the syntheses of phosphorus heterocycles. The characterization of a new family of compounds such as those derived from 5-aza-2,8-dioxa-1-phospha^{V}-dibenzo-[c,f]bicyclo-[3.3.0]octadiene in which the phosphorus substituents are X = chlorine **1**, methyl **2**, methoxy **3**, isopropylamine **4**, *n*-butylamine **5**, *sec*-butylamine **6**, *tert*-butylamine **7**, 2-aminopyrimidine **8**, glycol **9**, catechol **10**, 3,5-di-*tert*-butylcatechol **11**, *o*-aminophenol **12**, and phenylenediamine **13** is reported. The phosphorane system 10-P-5 of compounds **1–13** has been characterized by ^{1}H, ^{13}C and ^{31}P NMR, IR, and mass spectra. The structure of compound **4** was determined by X-ray diffraction. Phosphoranes **1–8** have an aromatic, planar tetracyclic structure, in which the phosphorus atom is a trigonal bipyramid with the oxygen atoms in axial positions. Compounds **9–13** have the diphenolamine ligand in a folded conformation with two oxygen atoms in equatorial and the nitrogen in axial position.

Key words: NMR, X-ray diffraction, dibenzobicyclic phosphoranes 10-P-5.

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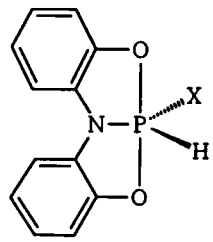
INTRODUCTION[1]

In previous reports we have described the synthesis and structures of pentacoordinated phosphorus compounds 10-P-5,[2,3] derived from diphenolamine, (Figure 1). The dibenzophosphoranes have a phosphorus atom with a trigonal bipyramid ge-

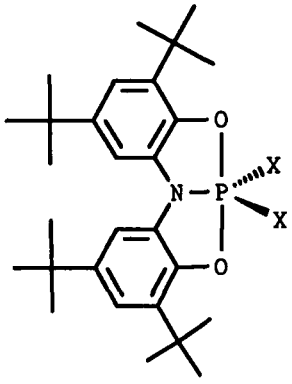


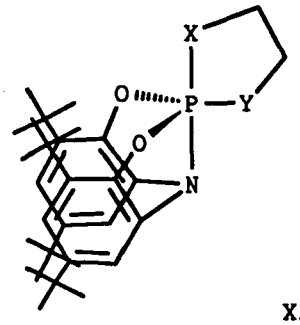
X= C_6H_5, H, OR, NHR

FIGURE 1

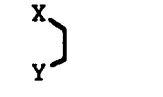
ometry (tbp) in a rigid tetracyclic framework[2,3] as determined by X-ray diffraction studies. Bicyclic dibenzophosphoranes were found to be more stable than their aliphatic analogs,[4–7] this stability is attributed to the rigidity of the framework in the diphenolamine phosphoranes which precludes tautomerization P(5)—P(3)[2a] by opening the P—N bond.[7]

Herein, we report the synthesis of another family of phosphoranes bearing the backbone 5-aza-2,8-dioxa-1-phospha^{V}-dibenzo[c,f]bicyclo[3.3.0]octadiene in which the X group at the P atom are: chlorine **1**, methyl **2**, methoxy **3**, isopropylamine **4**, *n*-butylamine **5**, *sec*-butylamine **6**, *tert*-butylamine **7**, 2-aminopyrimidine **8**, glycol **9**, catechol **10**, 3,5-di-*tert*-butylcatechol **11**, *o*-aminophenol **12**, and phenylenediamine **13** (Figure 2). The structure of compounds **1–13** has been deduced from the ^{31}P, ^{13}C and ^{1}H NMR spectra. Compound **4** has also been studied by X-ray diffraction. The similarity of the NMR spectra of compound **4** with **1–3** and **5–7**





1 X=Cl
2 X=CH_3
3 X=OCH_3
4 X=*iso*-PrNH
5 X=n-BuNH
6 X=*sec*-BuNH
7 X=*tert*-BuNH
8 X=$HNC_4H_3N_2$



9
10
11
12
13

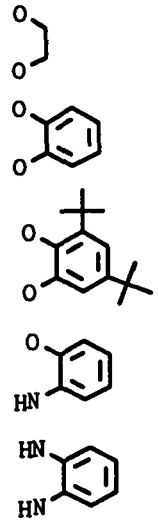


FIGURE 2

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led us to believe that all these compounds have the same structure in solution and the solid state.

RESULTS AND DISCUSSION

Compound 1

Compound **1** was prepared in two steps, the first afforded the *bis*[iminophenolate]zinc complex **14** from the reaction of 4,6-di-*tert*-butyl-catechol, ammonium hydroxide and zinc acetate.[8,9] Compound **14** has been previously used to prepare the tetra-*tert*-butyldiphenolamine ligand which in turn was employed to prepared some stiboranes and phosphoranes.[10] In this study the zinc compound **14** reacted directly with phosphorus trichloride in benzene to give quantitatively the dichloro-diben

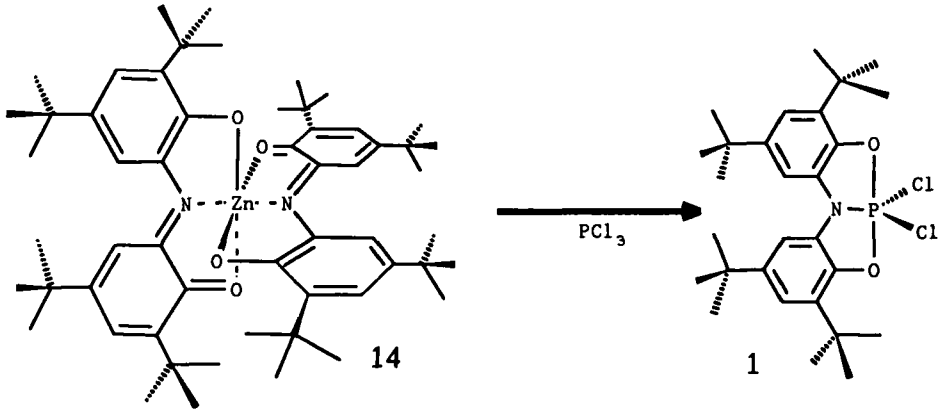
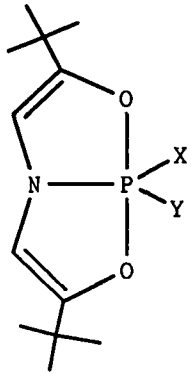


FIGURE 3



15a) X=Y=Cl ^{31}P δ=-24.9 ppm

15b) X=Y=CH_3 ^{31}P δ=-9.1 ppm

15c) X=Cl, Y=CH_3 ^{31}P δ=-0.8 ppm

FIGURE 4 ^{31}P NMR data of compounds **15a–15c**, Reference 11.

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zophosphorane 10-P-5 **1** (Figure 3), which was isolated as a pure stable solid in an inert atmosphere. Compound **1** has a single signal at ^{31}P $\delta = -20.4$ ppm indicative of a 10-P-5 bonding system, similar to dichlorophosphorane **15a** (Figure 4) prepared from the di-*tert*-butyldiketoamine[11] (^{31}P $\delta = -24.9$ ppm). The ^{1}H and ^{13}C NMR spectra show half of the total carbon atoms and protons which suggests a symmetric molecule, (Tables I–II). The X-ray diffraction studies of some bicyclic related phosphoranes derived from diphenolamine,[2,3] di-*tert*-butyl diketoamine,[11] and now the structure of compound **4**, show that the phosphorus is a trigonal bipyramid with the oxygen atoms in the axial and the nitrogen atoms in the equatorial position. The dichlorophosphorane **1** is a very reactive and also stable compound. In order to explore its usefulness for the syntheses of other phosphoranes we have reacted

TABLE I

^{13}C NMR chemical shifts and [J(C-P)] of aromatic carbon atoms

Compd	C1	C2	C3	C4	C5	C6
1	141.0[6]	126.6[28]	106.8[16][1]	145.0	116.9[2]	133.9[10]
2[a]	143.7[4]	129.1[19]	106.8[12][3]	141.6	115.4[4]	131.4[3]
3[b]	141.3[4]	128.5[4]	106.4[14]	142.3	115.8	132.0[3]
4[c]	s	130.0[21]	106.4[13]	142.2	114.9	131.3[5]
5[d]	s	130.1[21]	106.3[14]	142.2	114.9	131.2[5]
6[e]	s	130.1[9]	106.4[13]	142.2	114.9	131.3[5]
7[f]	142.3[4]	129.9[21]	106.1[13]	142.4	115.2	131.9[7]
8[g]	s	128.9[24]	106.1[14]	142.4	115.7	131.7[7]
9[h]	133.8[13]	133.3[20]	107.9[17]	145.3	115.4	138.5[3]
10[i]	134.7[12]	132.9[20]	108.0[14]	144.3	116.3	137.8[5]
11[j]	134.7[12]	133.3[20]	108.0[14]	144.1	116.3	138.0[3]
12[k]	134.8[13]	130.2[18]	109.5[14]	145.3	116.7	139.0[6]
13[l]	134.8[12]	128.4[6]	110.1[14]	145.2	116.5	139.1[6]
14	178.6	137.4	116.4[7]	144.9	131.7[8]	142.5

1) $^{1}J(C-H)$= 158, $^{3}J(C-H)$= 8; 2) $^{1}J(C-H)$= 155, $^{3}J(C-H)$= 7 Hz; 3) $^{1}J(C-H)$= 156, $^{3}J(C-H)$= 8; 4) $^{1}J(C-H)$= 154, $^{3}J(C-H)$= 7 Hz; 5) not observed, could be under the signal of C4. 6) hidden by the C_6D_6. 7) $^{1}J(C-H)$= 157, 8) $^{1}J(C-H)$= 131.9 (a) P-CH_3 22.5[128], $^{1}J(P-C)$=130 Hz. b) OCH_3 55.9[10]. c) NCH 31.7[7], CH-$\underline{CH}_3$ 25.9[6.6]. d) n-Bu: α 43.49, β 34.86, γ 20.21, δ 13.89. e) *sec*-Bu: α=49.82, β CH_3= 23.47 and 23.42, β CH_2 23.42 and 23.47, γ CH_3 10.36 and 10.20. f) N-C 51.02 $^{2}J(C-P)$= 2, NCCH_3 31.81 $^{3}J(C-P)$= 5.5, g) 2-aminopyrimidine C'*i*-160.75 $^{2}J(C-P)$=4, C'*m*-157.8, C'*p*-114.0, h) CH_2 63.45 $^{2}J(C-P)$= 3, i) catechol: C'-1 144.9 $^{2}J(C-P)$= 5.4, C'-2 111.5 $^{3}J(C-P)$= 16, C'-3 122.4. j) the data of 3,5-di-*tert*-butylcatechol were not assigned. k) *o*-aminophenol: C'-1 146.6, C'-2 136.0 [15], C'-3 110.4[18], C'-4 121.7, C'-5 110.5[14], C'-6 120.24. l) Phenylenediamine: C'-2 137.1[15], C'-3 113.36, C'-4 120.3.

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TABLE I (*Continued*)

^{13}C NMR δ of *tert*-butyl carbon atoms

Compd	C-7	C-8	C-9	C-10	Compd	C-7	C-8	C-9	C-10
1	35.1	31.7[1]	34.6	29.7[2]	**8**	35.0	32.1	34.4	29.7
2	34.9	32.1[3]	34.5	29.6[3]	**9**	35.0	32.0	34.9	30.0
3	35.0	32.0	34.6	30.0	**10**	35.0	31.7	34.6	29.7
4	34.9	31.2	34.2	30.2	**11**	35.0	31.8	34.7	29.8
5	34.8	32.0	34.6	30.3	**12**	35.0	31.8	34.7	29.7
6	34.9	32.0	34.5	30.2	**13**	35.0	31.9	34.7	29.9
7	34.8	32.0	34.5	30.5	**14**	35.3	30.0[4]	34.6	29.1[5]

1) $^1J(C-H)$= 130 Hz 2) $^1J(C-H)$= 131 Hz 3) $^1J(C-H)$= 125 Hz 4) $^1J(C-H)$= 126.7 Hz 5) $^1J(C-H)$= 127.8 Hz.

TABLE II

^1H NMR δ of compounds **1–14**

Compd	H-3	H-5	H-8	H-10	Compd	H-3	H-5	H-8	H-10
1	7.67	7.28	1.44	1.62	**8**[g]	7.88	7.18	1.44	1.61
2[a]	7.93	7.23	1.53	1.60	**9**[h]	7.57	7.15	1.36	1.52
3[b]	7.83	7.21	1.44	1.58	**10**[i]	7.64	7.18	1.40	1.43
4[c]	7.79	7.5	1.42	1.56	**11**[j]	7.62	7.12	2	2
5[d]	7.79	1	1.42	1.57	**12**[k]	7.62	7.12	1.40	1.42
6[e]	7.80	7.15	1.42	1.57	**13**[l]	7.62	7.26	1.40	1.41
7[f]	7.83	7.18	1.40	1.62	**14**	7.28	7.09	1.73	1.83

1) not observed, 2) not assigned a) $P-CH_3$ 2.09, $^2J(H-P)$=15 b) OCH_3 3.52, $^3J(P-H)$= 4.5. c) NH 2.59 d,d $^2J(P-H)$=13, $^3J(H-H)$=8, NCH 3.81 (complex), $NCH-C\underline{H}_3$1.1 d,d $^4J(P-H)$= 1.5, $^3J(H-H)$= 6. d) n-Bu: N-H 2.6, d,t $^2J(H-P)$ = 13, $^3J(H-H)$ = 1.98, α = 3.04, β =1.30, γ=1.18, δ=0.74 t, ^3J= 7Hz. e) *sec*-Bu: N-H 2.56, d,d, $^2J(P-H)$= 13, $^3J(H-H)$=8.7, NCH 3.66 (complex), NC-CH3 1.01 and 1.00, both $^3J(H-H)$ =6.4, NCCH2 1.3 (complex), NCCCH3 0.76 $^3J(H-H)$=7.5. f) N-H 2.98 $^2J(H-P)$=12.5, N-*tert*Bu 1.26 $^4J(H-P)$= 1.3 Hz. g) 2-aminopyrimidine: N-H 7.61 $^2J(H-P)$= 10, H*m* 7.84 d, $^3J(H-H)$= 4.85, H*p* 5.92 t $^3J(H-H)$=4.85. h) OCH_2 3.64d i) catechol: H'3 6.90 (complex) H'4 6.64 d,d, $^3J(H-H)$= 6.5 $^4J(H-H)$= 3.5. j) the data of 3,5-di*tert*butylcatechol were not assigned. k) *o*-aminophenol H'-3 6.38, H'-4 6.74, H'-5 6.70, H'-6 7.40 (complex multiplets), l) phenylenediamine: 6.42 H'-3 6.42, H'-4 6.74 (complex multiplets).

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TABLE III

^{31}P NMR of **1–13** in C_6D_6[a] [$^nJ_{PH}$ (Hz)]

comp.	^{31}P(ppm)	$^nJ_{PH}$ (Hz)
1	-20.4	
2	-7.8	^2J=14.6
3	-38.3	^3J=14.6
4	-46.2	^2J=13.2
5	-43.3	^3J=12.2
6[b]	-45.3	complex
	-45.4	
7	-42.1	^2J=12.4
8	-46.5	
9	-16.0	
10	-14.5	
11	-14.7	
12	-21.3	^2J=22.9
13	-27.2	

a) δ in ppm (external reference 85% H_3PO_4)
b) diasteromeric mixture

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it with methyl lithium and different compounds bearing acidic protons. A discussion of the reactions and products follows.

Compound **2**

The reaction of compound **1** with 2-equivalents of MeLi in benzene produced the dimethylphosphorane **2**. The reaction was monitored by ^{31}P NMR and is quantitative. The new compound showed an heptuplet at ^{31}P δ −7.8 ppm, by coupling with the methyl protons (^2J(P—H) = 14.6 Hz). The methyl groups appear at ^1H δ = 2.08 ppm (^2J(H—P = 14.6 Hz) and at ^{13}C δ = 22.5 ppm (^1J(C—P) = 127.8 Hz), (Tables I–III). When the reaction was carried out in a deficit of methyllithium some monomethylmonochloride phosphorane was observed at ^{31}P δ = −15.6 ppm. The ^{31}P δ of compounds **1** and **2** are in agreement with those reported by Arduengo for similar compounds (**15a–15b**, Figure 4) of tbp structure,[11] but we disagree with that of **15c**, we think that its value must be near the average of those of **15a** and **15b** (−17 ppm).

Compound **3**

The phosphorane dimethylester **3** was prepared from **1** and two equivalents of dry methanol. The ^{31}P NMR resonance presents an heptuplet at δ −38.3 ppm (^3J(PH) = 14.6 Hz), corresponding to a tetraoxyphosphorane. The ^{13}C NMR spectrum shows a great similarity with that of compound **2**, a double signal at 55.9 ppm (^2J(POC) = 9.9 Hz) was attributed to the methyl groups. The ^1H NMR resonance shows the methoxy group at δ 3.73 ppm (^3J(H—P) = 14.6 Hz), Table I. The synthesis of compound **3** was mentioned by Stegmann, but without spectroscopic data.[12]

Compounds **4–8**

Reaction of compound **1** with four equivalents of different primary amines (*iso*-propylamine, *n*-butylamine, *sec*-butylamine, *tert*-butylamine and 2-aminopyrimidine), gave the corresponding amides **4–8**. In all cases the reactions were quantitative and were monitored by ^{31}P NMR, the phosphorane signals were found around $\delta = -42$ to -47 ppm, (Table III). The phosphorane derived from racemic *sec*-butylamine **6** gave two signals in ^{31}P NMR spectrum owing to a diastereomeric mixture.

We were able to obtain single crystals for **4**, and the X-ray diffraction structure was obtained (Figure 5). There are two phosphorane molecules in the asymmetric unit, there are no significant differences between the two for clarity we will discuss only one (Figure 6); Table V contains the crystal data, positional parameters are in Table VI, selected interatomic distances and bond angles are in Table VII and selected torsion angles are in Table VIII. The phosphorus molecule is near that of a perfect tbp geometry [O—P—O, 175.8(3); N14—P1—N18, 120.5(3); N7—P1—N14, 121.1(3); N7—P1—N18, 118.1(3)Å] with the oxygen atoms in apical positions. The tetracyclic framework is not completely planar, one of the phosphorus rings (de-

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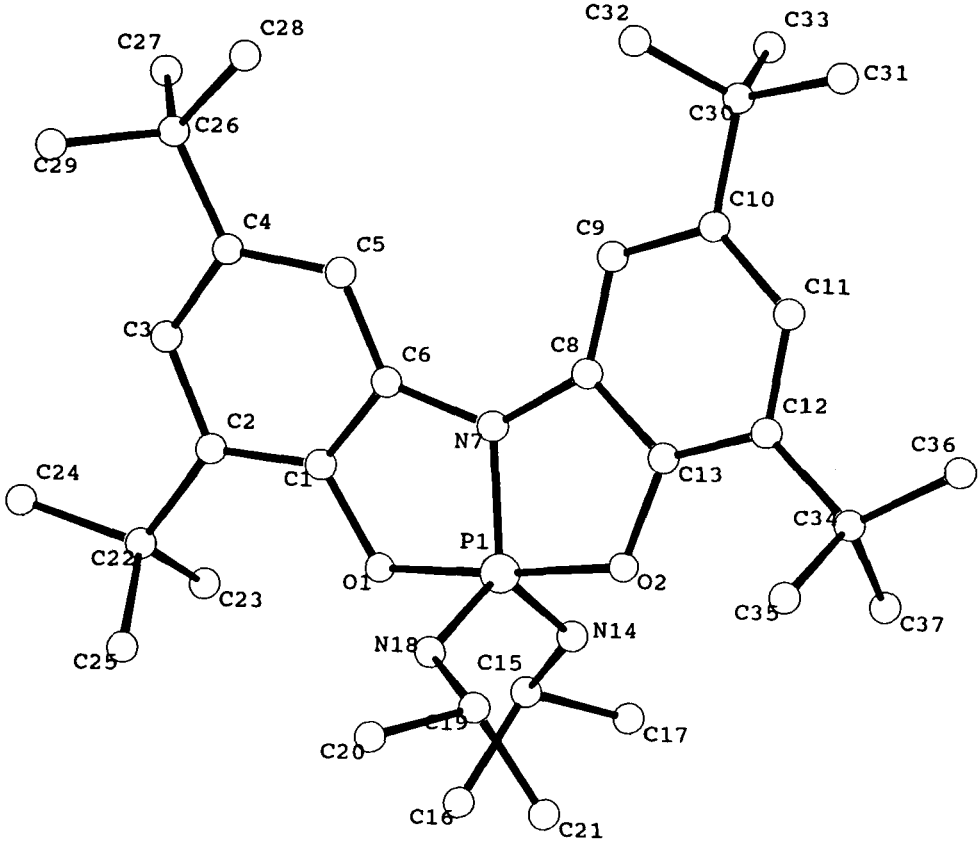

FIGURE 5 X-ray diffraction structure of compound **4**.

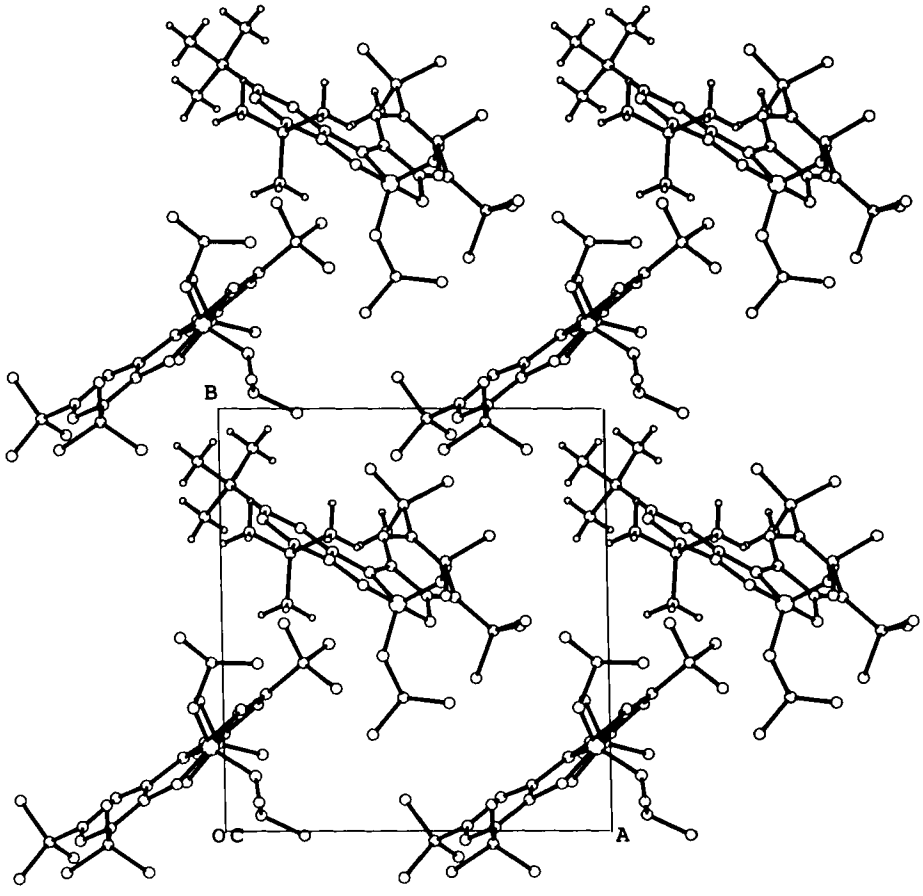

FIGURE 6 Unit cell of compound **4**.

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TABLE IV

Solid state IR frequencies of **1–13** (cm^{-1}, KBr)

comp.	N-H	P-N		P-O[a]
1		1066	900	1242
2			982	1246
3			990	1246, 1078
4	3442	1064	986	1242
5	3432	1064	988	1244
6	3458	1064	902	1248
7	3430	1064	984	1248
8	3352	1066	988	1244
9		1050	972	1240, 1062
10		1096	1034	1262
11		1062	1062	1228
12	3378	1056	938	1246
13	3426	1052	914	1230

a) belong to P-O-aryl

TABLE V

CRYSTAL DATA for	$C_{34}H_{80}N_3O_2P$
fw	594.01
space group	P -1
a (Å) =	11.805 (1)
b (Å) =	13.184 (1)
c (Å) =	23.296 (1)
α (°) =	76.32 (3)
β (°) =	83.95 (6)
γ (°) =	89.39 (6)
V ($Å^3$)	3503.1 (1)
Z	4
F(000)	1344
systematic absences	none
Diffractometer	CAD4-Enraf-Nonius
radiation	MoKα (λ =.71069 Å)
linear abs coeff cm^{-1}	1.1
ρ (calc) g cm^{-3}	1.13
scan type	ω/2θ
scan range (°)	0.5 + 0.78 tg θ
θ limits (°)	1 - 25
temperature of measurement	-88°C
no of unique data collected	10080
no of unique data used	5934 $(Fo)^2 > 3\sigma (Fo)^2$
decay %	<1
absorption coeff.	0.787>coeff>1.12
R =Σ||Fo| - |Fc||)/Σ |Fo|	0.088
Rw =$[\Sigma w(\|Fo\| - \|Fc\|)^2/\Sigma wFo^2]^{1/2}$	0.096
Goodness of fit s	2.76
no. of variables	721
Δρmin (e/$Å^3$)	-.57
Δρmax (e/$Å^3$)	.47

picted by P1—N7—C8—C13—O2 and its phenyl fragment is in a plane, the other part of the molecule is slightly folded as can be appreciated from the torsion angles (O2—P1—O1—C1 36.73). The three nitrogen atoms are also planar indicating a retrocoordination to the phosphorus atoms as is supported by the short distances P1—N7 [1.713(6) Å], P1—N14 [1.648(7)Å]; P1—N18 (1.661(6) Å] not very far from a typical P=N double bond (1.60 Å)[13]; the P—O bonds are typical axial single bonds P1—O1 (1.693 Å).[13]

Compounds **9–13**

Addition of a bidentate ligand to phosphorane **1** afforded a different structure from that of compounds **1–8** as it was deduced from the significant change in their ^{31}P and ^{13}C NMR spectra. Analogous structures derived from *o*-chloranil **16**[4] and **17**[11] have been reported, (Figure 7). The addition of new five membered ring to the

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TABLE VI

Positional parameters and their estimated standard deviations

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) \cdot [a^2 \cdot B(1,1) + b^2 \cdot B(2,2) + c^2 \cdot B(3,3) + ab(\cos\gamma) \cdot B(1,2) + ac(\cos\beta) \cdot B(1,3) + bc(\cos\alpha) \cdot B(2,3)]$

Atom	x	y	z	B(A2)
P1	0.9631(2)	0.2005(2)	0.79622(8)	2.60(4)
O1	1.0442(4)	0.2884(3)	0.7432(2)	2.8(1)
O2	0.8740(4)	0.1125(4)	0.8462(2)	2.8(1)
N7	0.8916(4)	0.1753(4)	0.7408(2)	2.4(1)
N14	0.9209(5)	0.2919(5)	0.8309(3)	3.1(1)
N18	1.0782(5)	0.1312(5)	0.8137(2)	3.0(1)
C1	1.0374(6)	0.2778(5)	0.6862(3)	2.3(1)
C2	1.1100(6)	0.3248(5)	0.6375(3)	2.4(1)
C3	1.0879(6)	0.3005(5)	0.5835(3)	2.8(2)
C4	1.0011(6)	0.2319(5)	0.5796(3)	2.6(2)
C5	0.9295(6)	0.1846(5)	0.6314(3)	2.4(1)
C6	0.9481(5)	0.2106(5)	0.6843(3)	2.3(1)
C8	0.7953(5)	0.1090(5)	0.7602(3)	2.2(1)
C9	0.7154(5)	0.0803(5)	0.7272(3)	2.4(1)
C10	0.6263(5)	0.0122(5)	0.7578(3)	2.7(2)
C11	0.6199(6)	-0.0215(6)	0.8196(3)	3.0(2)
C12	0.6992(5)	0.0089(5)	0.8541(3)	2.5(2)
C13	0.7873(5)	0.0743(5)	0.8217(3)	2.2(1)
C15	0.9697(6)	0.3989(6)	0.8219(3)	3.3(2)
C16	1.0887(7)	0.3968(7)	0.8430(4)	5.0(2)
C17	0.8890(8)	0.4572(7)	0.8570(4)	5.0(2)
C19	1.0910(6)	0.0382(6)	0.8623(3)	3.6(2)
C20	1.2037(8)	-0.0102(7)	0.8466(5)	6.2(3)
C21	1.0861(8)	0.0691(8)	0.9215(4)	5.5(2)
C22	1.2082(6)	0.3979(5)	0.6418(3)	3.1(2)
C23	1.1597(7)	0.4907(6)	0.6645(4)	4.2(2)
C24	1.2754(7)	0.4426(7)	0.5798(4)	4.7(2)
C25	1.2920(7)	0.3370(7)	0.6839(4)	4.7(2)
C26	0.9843(6)	0.2090(6)	0.5195(3)	2.9(2)
C27	0.9363(9)	0.3083(7)	0.4800(4)	5.4(2)
C28	0.8994(7)	0.1174(6)	0.5265(4)	4.8(2)
C29	1.0977(7)	0.1822(8)	0.4892(4)	5.4(2)
C30	0.5396(6)	-0.0234(6)	0.7211(3)	4.4(2)
C31	0.4599(7)	-0.1109(7)	0.7586(4)	5.8(2)
C32	0.6010(9)	-0.062(1)	0.6710(4)	10.2(3)
C33	0.4670(9)	0.0748(9)	0.6972(5)	9.4(3)
C34	0.6922(6)	-0.0311(6)	0.9217(3)	3.2(2)
C35	0.7971(7)	-0.0971(7)	0.9381(3)	3.8(2)
C36	0.5827(7)	-0.0973(7)	0.9459(4)	4.7(2)
C37	0.6903(8)	0.0629(7)	0.9512(4)	4.7(2)

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TABLE VII

Selected interatomic distances (Å) and bond angles (deg.)

P1-O1	1.698(4)	O1-C1	1.376(8)	N14-C15	1.409(9)
P1-O2	1.714(4)	O2-C13	1.375(8)	N18-C19	1.478(9)
P1-N7	1.713(6)	N7-C6	1.387(8)	C1-C6	1.400(1)
P1-N14	1.648(7)	N7-C8	1.409(8)	C8-C13	1.391(9)
P1-N18	1.661(6)				
O1-P1-O2	175.8(3)	N7-P1-N14	121.3(3)	C6-N7-C8	130.2(6)
O1-P1-N7	87.8(2)	N7-P1-N18	118.1(3)	P1-N14-C15	128.1(5)
O1-P1-N14	91.2(3)	N14-P1-N18	120.5(3)	P1-N18-C19	129.9(5)
O1-P1-N18	90.3(2)	P1-O1-C1	114.0(4)	O1-C1-C6	111.3(5)
O2-P1-N7	88.3(2)	P1-O2-C13	114.3(4)	O2-C13-C8	112.8(5)
O2-P1-N14	89.6(3)	P1-N7-C6	113.9(4)		
O2-P1-N18	92.9(2)	P1-N7-C8	115.1(4)		

TABLE VIII

Selected torsion angles (deg.)

O2-P1-O1-C1	-36.73	O2-P1-N7-C8	5.61
O1-P1-O2-C13	14.85	P1-O1-C1-C6	11.85
N7-P1-O1-C1	-15.99	P1-O2-C13-C8	4.86
N7-P1-O2-C13	-5.88	P1-N7-C6-C1	-12.99
O1-P1-N7-C6	16.49	P1-N7-C8-C13	3.99

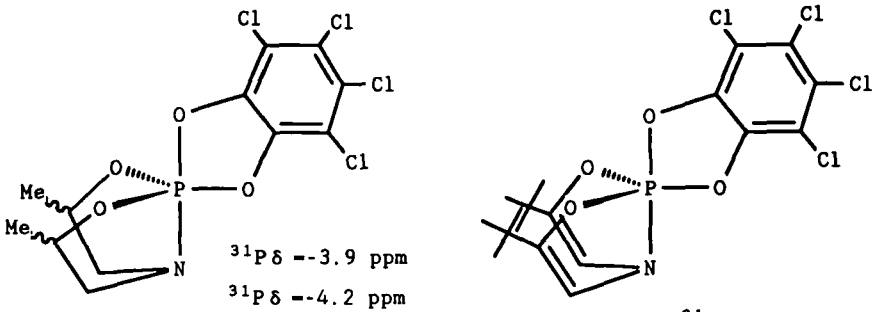

FIGURE 7

tetracyclic framework of phosphoranes precludes the equatorial-equatorial position for the new five membered ring, because it must correspond to an isomer of higher energy.[44] Therefore, the favored structure has the five membered ring in the axial-equatorial position which in turn makes the diphenolaminebicyclic framework change to a folded arrangement with the oxygen atoms in equatorial and the nitrogen

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in axial position.[11] Esterification with glycol, catechol, 4,6-di-*tert*-butyl-catechol, *o*-aminophenol, phenylenediamine of **1** gave the corresponding pentacyclic phosphoranes, **9–13**. The ^{31}P NMR resonances were found between -14.5 and -27.2 ppm. These values are shifted around 20 ppm to high frequency with respect to the corresponding planar phosphoranes. As observed for the glycol **9** ($\delta = -16.0$ ppm) and catechol derivatives **10** ($\delta = -14.5$ ppm) and **11** ($\delta = -14.7$ ppm) compared with the dimethoxy phosphorane **3** ($\delta = -38.3$ ppm) or the diphenylenediamine derivative **13** ($\delta = -27.2$ ppm) compared with the diamine phosphoranes **4–8** (δ -46.5 to -42.1 ppm). This fact can be explained by a better electron donating capacity of the oxygen atoms in equatorial (compounds **9–13**) than in axial position (compounds **1–8**). The ^{31}P chemical shifts are quite systematic as observed for the *o*-aminophenol phosphorane (**12**) chemical shift ($\delta = -21.3$) which correspond to the average of the chemical shift of catechol (**10**, $\delta = -14.7$) and phenylenediamine (**13**, $\delta = -27.2$) phosphoranes. In order to have more examples of this kind of phosphoranes we have tried to obtain the phosphorane derived from thioaminophenol, but were unable to obtain a pure compound, anyway, we have recorded its ^{31}P NMR ($\delta = -8.0$) and mass spectra MS M^+576.30(12). In general compounds **9–13** were found more sensitive to hydrolysis than **1–8**.

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Mass Spectra

In all cases phosphoranes **1–13** presented the M^+ molecular ion indicating very stable structures. And in some cases the naked tetracyclic framework (M 453.40). In compounds **9–13** the M^+ molecular ion was the parent peak (100%). The zinc complex did not show the molecular ion only the peak for the free ligand.

Infrared Spectra

Some regular features of the IR spectra, led us to make assignments for the bands of P—O, P—N and N—H bonds which are in Table IV.

Hydrolysis Products

In some reactions when the solvent was not completely dried, we have observed traces of other compounds accompanying the phosphoranes, attributed to hydrolysis products. In order to confirm it, we decided to investigate the behavior of compound **1** with one equivalent of H_2O and to follow the reaction by ^{31}P NMR. The spectra showed two important signals, one at -39.6 which slowly disappears and another at $+18.1$ which is the final product of the controlled hydrolysis. Both signals correspond to that occasionally observed at the different spectra of the phosphoranes reported here. The signal at -39.6 ppm was assigned to the phosphoranic acid **18** (Figure 7), because its chemical shift is similar to that of compound **3** ($\delta = -38.3$ ppm). The other singlet ($\delta = +18.1$ ppm) corresponds to a cyclic phosphate without a P—H bond, and it was not fully characterized. Another small signal was detected in the hydrolysis mixture with a $\delta = -14.7$ which was attributed to compound **19**, the reaction product of **1** with the diphenolamine liberated by hydrolysis of **1**. Compound **19** is similar to compound **12**, (Figure 8). Other small

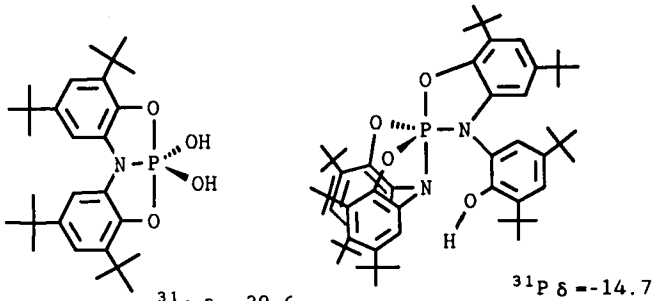
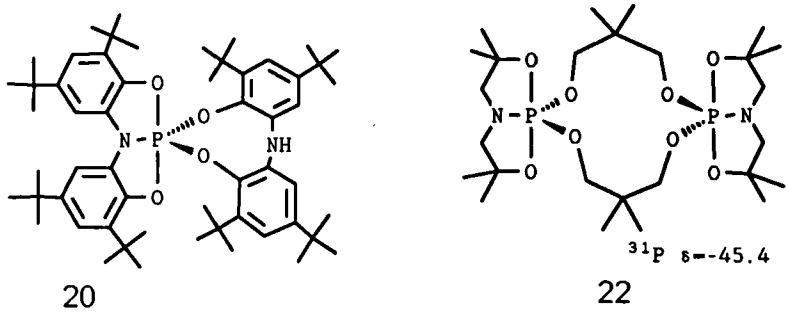


FIGURE 8



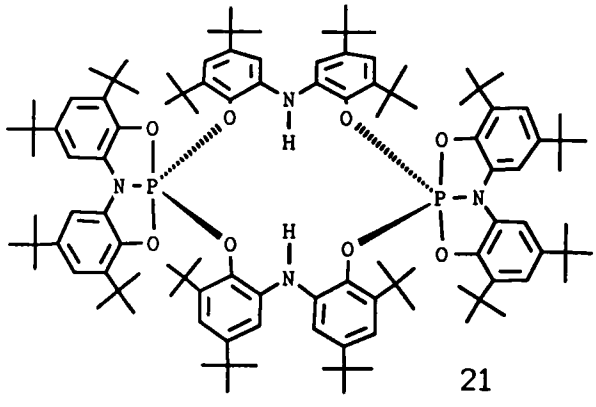


FIGURE 9

peaks around −45 ppm could correspond to compounds **20** or **21**, its structure was related to reported compound **22**[15–17] (Figure 9).

CONCLUSION

A new synthetic path to dibenzophosphoranes is described, which is a very simple procedure with high yields, and allows assembly of the organic molecule at the

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same time. The direct substitution of the metal atom by the phosphorus could have application in other coordination compounds. Owing to the stability and the easy substitution of the phosphorus substituents, especially the dichloro- **1** or the diamino- **(4–8)** phosphoranes it is evident that these new compounds are convenient reagents for building other phosphorus structures. We are currently investigating this behaviour.

EXPERIMENTAL

The reactions were carried out under an atmosphere of dry nitrogen. All solvents were freshly distilled and dried before use according to established procedures. Melting points were measured on a Gallenkamp apparatus and are uncorrected. The IR spectra were taken in KBr disc using a Perkin Elmer 16F PC IR spectrometer. All the NMR spectra were obtained on a JEOL GXS-270 spectrometer in C_6D_6 solution. ^1H and ^{13}C NMR spectra were measured with TMS as internal reference and ^{31}P NMR spectra are referenced to external 85% H_3PO_4. Mass spectra were obtained on a Hewlett-Packard HP 5989A. Elemental analyses were performed by Oneida Research, Services.

Crystal Structure Determination

Some experimental details are given in Table V. The crystal was mounted in a capillary tube. The data collection was first carried out at room temperature but atom vibration in the *tert*-butyl groups was very large. The data was therefore collected again at low temperature. However even then atomic vibration precluded a complete analysis and hydrogen atoms could not either found or placed in calculated positions. All calculations were carried out in a Vax 4000 computer using the Molen package.[18]

3,5-di-tert-butyl-1,2-quinone-1-(2-hidroxy-3,5-di-tert-butylphenol) imine zinc complex **14**: Compound **14** was prepared by the established literature procedure.[8] MS(EI, 300°C) m/e 425.55(100), 422.55(31).

1,1dichloro-5-aza-2,8-dioxa-1-phospha^V-dibenzo[9,9',11,11'-tetra-tert-butyl]-bicyclo[3.3.0]]octadiene **1**: A solution of 0.228 g (0.25 mmol) of zinc complex **14** in 3 ml of dry benzene was treated dropwise at room temperature under vigorous stirring with PCl_3 (0.343 g, 2.5 mmol). Additional stirring for 2 h affords a solution. The $ZnCl_2$ formed was filtered and the volatile materials were removed at reduced pressure to leave a white solid **1** in quantitative yield, mp 222°C. NMR ^1H, ^{13}C and ^{31}P (Tables I, II and III), Anal. Calc. for $C_{28}H_{40}Cl_2NO_2P$: C, 64.12; H, 7.68; N, 2.67. Found C, 64.88; H, 7.76; N, 2.54. MS(EI, 300°C) ^+M 527.30(7), 526.30(10), 525.30(36), 524.3(16), 523.3(51), 510.3(15), 508.3(23), 454.45(10).

1,1-dimethyl-5-aza-2,8-dioxa-1-phospha^V-dibenzo[9,9',11,11'-tetra-tert-butyl]-bicyclo[3.3.0]octadiene **2**: The compound **1** (1 mmol scale) is dissolved in 3 ml of THF and 2 eq. of MeLi in ether were added to this solution at 0°C. After stirring 1 h more at the same temperature. The solution was filtered and the solvent was evaporated at reduced pressure to leave a yellow solid, in quantitative yield, mp, (110–115°C dec). MS(EI, 300°C), M^+ 483.5(32), 484.5(11) 468.50(15).

1,1-dimethoxy-5-aza-2,8-dioxa-1-phospha^V-dibenzo[9,9',11,11'-tetra-tert-butyl]bicyclo[3.3.0]octadiene **3**: Compound **1** (1 mmol scale) is dissolved in 3 ml of THF and 2 eq. of dry MeOH were added at room temperature. After stirring for 15 min the solution was filtered and removal of the volatiles in vacuo left a white solid in quantitative yield, mp 168–169.5°C. Anal. Calc. for $C_{30}H_{46}NO_4P$: C, 69.93; H, 8.98; N, 2.71. Found C, 69.01; H, 8.64; N, 2.42. MS(EI, 300°C), M^+ 515.45(100), 516.45(30), 500.45(39), 469.45(6), 454.45(5).

1,1-diamines derivatives of 5-aza-2,8-dioxa-1-phospha^V-dibenzo[9,9',11,11'-tetra-tert-butyl]-bicyclo[3.3.0]octadiene (**4**, *iso-propylamine;* **5**, *n-butyl-amine;* **6**, *sec-butylamine;* **7**, *tert-butylamine;* **8**, *2-aminopyrimidine*): Compound **1** (1 mmol scale) is dissolved in 3 ml of dry benzene and four eq. of the corresponding amine were added to this solution at room temperature. After stirring 2 h the solution was filtered and the solvent was evaporated at reduced pressure, in all cases a solid was obtained in quantitative yield. Compound **4**, mp. (130–132°C dec). MS(EI, 300°C) M^+ 569.50 (100), 570.50(44) Compound **5**, mp. (46–48°C dec). MS(EI, 300°C) M^+ 597.65 (100), 598.50(41), 453.40(3). Compound **6**, mp. (72–75°C). MS(EI, 300°C) M^+ 597.50 (100), 598.50(40), 453.45(14). Compound **7**, mp. (85–90°C dec). MS(EI, 300°C) M^+ 597.65 (2). Compound **8**, mp. (115°C dec). MS(EI, 300°C) M^+ 469.55 (100), 454.50(25).

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Ethyleneglycol (**9**), *1,2-catechol* (**10**), *3,5-di-tert-butylcatechol* (**11**), *aminophenol* (**12**) *and 1,1-phenylenediamine* (**13**) *derivatives of 5-aza-2,8-dioxa-1-phospha^{V}-dibenzo[9,9',11,11'-tetra-tert-butyl]-bicyclo[3.3.0]-octadiene*: Compound **1** (1 mmol scale) is dissolved in 3 ml of dry benzene and 1 eq. of the corresponding reagent in 5 ml of dry benzene was added solution at rt. After stirring 24 h, the solution was filtered and the solvent was evaporated at reduced pressure, the reaction products were solid obtained in quantitative yield. **9** mp. (192–193°C dec). MS(EI, 300°C) M^+ 513.50(3) **10** mp. (136–138°C dec). MS(EI, 300°C) M^+ 561.50(13). **11** mp. (252–255°C dec). MS(EI, 300°C) M^+ 673.70(100), 674.70(51) **12** mp. (78–80°C dec). MS(EI, 300°C) M^+ 560.30(100), 561.30(37). **13** mp. (134–136°C dec). MS(EI, 300°C) M^+ 559.55(100), 560.55(37).

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